

(METH) ACRYLIC ESTER DERIVATIVES

This is a division of application Ser. No. 08/378,245 filed Jan. 24, 1995 abandoned.

BACKGROUND OF THE INVENTION**1. Field of the Invention**

The present invention relates to (meth)acrylic ester derivatives having a disulfide cyclic group. The (meth) acrylic ester derivatives may be used as precious metal adhesive components in dental and other medical industry areas, as well as in general industrial areas including the art of jewelry.

2. Description of the Prior Art

Hitherto, for use as a resin-based dental adhesive there have been known compounds which are composed principally of an instantaneously polymerized resin made up of poly(methyl methacrylate) and methyl methacrylate or a methacrylic ester called Bis-GMA resin, with a filler and a hardener used in admixture with the resin. Such compounds, as so-called dental adhesive resins, have been used for various clinical dental purposes, such as metal inlaying, onlaying, crowning and bridging, and adhesive fixation with respect to dental orthodontic brackets, metal bases, etc.

Monomers having an adhesive function which may be advantageously incorporated in Such adhesive resins are known including, for example, (meth)acrylic ester derivatives having a phosphoric group as described in Japanese Patent Application Laid-Open No. Sho 58-21607, which teaches that the (meth)acrylic ester derivatives provide improved metal adhesion.

Japanese Patent Application Laid-Open No. Sho 54-11149 discloses that 4-methacryloxyethyl trimellitate or the anhydride derivative thereof can enhance resin adhesion with metals.

However, it has been known that although the compounds disclosed in the above mentioned publications are effective for improving adhesion with non-precious metals, such as iron, aluminum, copper, tin, nickel, chromium, cobalt and titanium, and alloys thereof, their adhesion performance is very unfavorable in relation to precious metals, such as gold, silver, platinum and palladium, and alloys thereof. Therefore, from clinical points of view, it is very troublesome to carry out an electrodeposition of tin or high temperature oxidative treatment with respect to precious metals and/or their alloys, though such a way of deposition or oxidative treatment is currently in practice.

Recently, it has been proposed to provide increased adhesivity relative to precious metals by using a treating agent which contains a certain type of monomer having adhesive functions.

For example, in a dental journal *The Journal of the Japanese Society for Dental Materials and Devices*, vol. 5, pp 92-105 (1986), it is reported that a treating agent containing N-(4-mercaptophenyl)methacrylamide (hereinafter referred to as MPMA) can improve resin adhesion with any precious metal.

In Japanese Patent Application Laid-Open No. Sho 64-83254 there is given a teaching that polymerizable double bond-containing derivatives of 1, 3, 5-triazine-2, 4-dithione and, in particular, 6-(4-vinylbenzyl-n-propyl)amino-1, 3, 5-triazine-2, 4-dithione (hereinafter referred to as VBATDT), are highly effective for improving resin adhesion with precious metals and their alloys. However, both MPMA and VBAT can only provide a very low degree of adhesion

where a BPO/amine-based polymerization catalyst is used, and this poses a problem from the view point of retention of adhesion under demanding interoral conditions. Another problem is that MPMA has some deficiency in respect of storage stability.

Japanese Patent Application Laid-Open No. Sho 63-225674 teaches that polysulfide compounds, such as bis(2-methacryloyloxyalkyl) disulfide, exhibit good adhesion characteristics relative to precious metals. With primers containing such compounds, it has been found that their adhesion retentive power is very low when the primer is used in combination with general-purpose catalysts, such as benzoyl peroxide/tertiary amine, though it is recognized that the primer has some adhesion effect due to a certain polymerization catalyst which is present in an adhesive resin used in combination with the primer.

For example, in *The Journal of the Japanese Society for Dental Materials and Devices*, vol. 11, "Lecture Issue 20", pp 234-235 (1992), as well as in *The Journal of the Japanese Society for Dental Materials and Devices*, vol. 12, "Lecture Issue 21", pp 164-165 (1993), it is reported that bis(2-methacryloyloxyethyl) disulfide (hereinafter referred to as BMEDS), bis(5-methacryloyloxypropyl) disulfide (hereinafter referred to as BMPDS), and bis(10-methacryloyloxydecyl) disulfide (hereinafter referred to as BMDDS) function unfavorably in respect of adhesion with silver and silver alloys, say, 0 kgf/cm² with silver and as low as 106-289 kgf/cm² with silver alloys when benzoyl peroxide/tertiary amine catalysts are used.

In Japanese Patent Application Laid-Open No. Hei 1-268612 there is disclosed that monomers having a thiophosphoric acid group, e.g., 10-methacryloyloxy decyl dihydrogen thiophosphate (hereinafter referred to as M10PS), exhibit very good adhesion with precious metals and outstanding adhesion retentive power when the monomer is used in a proportional range of from 0.001 to 0.3 part by weight. However, monomers having a thiophosphoric acid group as represented by M10PS involve a problem objectionable from the view point of practical use such that the monomer will tend to become decomposed during storage to produce terrible odors which are extremely displeasing to the clinician when he is working for dental adhesion.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a novel compound useful as a precious metal adhesive component which exhibits strong and permanent adhesion with precious metals, such as gold, silver, platinum, and palladium, without requiring the precious metals to be subjected to such pretreatment as electrodeposition of tin or oxidative treatment, and which can come into strong adhesion with any of the precious metals without being influenced by the type of polymerization catalyst used, has good storage stability and involves no generation of objectionable odors during the preparation thereof or when in use.

It is another object of the invention to provide a method for production of such a compound.

It is a further object of the invention to provide an adhesive comprising aforementioned novel compound as a precious metal adhesive component.

Accordingly, the invention relates to (meth)acrylic ester derivatives represented by the general formula [I]: